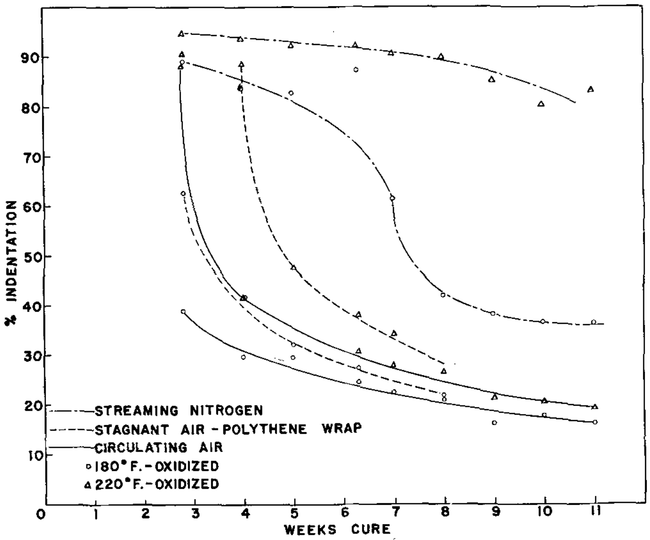

FIG. 8. Curing of linoleum binder in various atmospheres at 90°C.

vantages of this product are greater variety of design and better color. The wearing surface is about 3.5 to 5 mils thick, compared to 4 to 6 mils for printed felt-base. It is expected that this product will replace a substantial part of the drying-oil type.

A few general remarks may be made to compare the drying oil-based floor coverings with the synthetic resin ones. Linoleum could be improved in resistance to moisture, especially alkaline moisture as is present in concrete floors on grade, and in color, as the binder is inherently amber-colored. Polyvinyl chloride floor coverings could be improved in stability as the resin tends to degrade in light and air, in indentation resistance since it is thermoplastic, and in stain and soil resistance since the plasticizer tends to retain dirt. Polyvinyl chloride floor coverings are superior to linoleum in abrasion resistance although this is offset by the thinner wearing surface, in color and in water and in alkali resistance. They are limited by higher price, difficulty in retaining the original appearance, and by thermoplasticity.

If one wishes to increase the use of drying oils in floor coverings, it is obvious that improvements must be made in the drying-oil products. The comparisons just made can serve as a basis for a research program to use the chemistry of drying-oil systems to provide in the binder better water and alkali resistance, clear color, and rapid processing at low cost. With respect to costs the price of linseed oil, now about 14¢, is often compared with that of polyvinyl chloride at about 23¢. It would be more realistic, in my opinion, to compare linseed with vinyl chloride at 11¢, or ethylene at 5¢. Normally the conversion of monomeric drying oils to polymeric products is less expensive than the conversion of synthetic monomers so that some margin is available for new developments based on the application of polymer chemistry to drying oils. This is the only hope we see for increasing the use of drying oils in floor coverings.

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Degradation of Drying Oil Films

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THE NEED for an understanding of the processes of degradation has led to continued research in various academic and industrial laboratories. And whether the justification for such work is an increase in human knowledge or a more marketable product, there have been basically two approaches, one empirical and one analytical. Both are valid, useful, and even necessary, and together they have produced a consistent picture of the chemical reactions which produce degradation and the physical manifestations of these reactions.

The physical manifestations of deterioration of a particular film, polymerized linseed oil, are many: loss of gloss, erosion, yellowing, embrittlement, loss of adhesion, cracking, to mention a few. All are not equally important in every application, but all are the inevitable consequences of the same sequence of chemical reactions. Moreover these are the same chemical reactions which polymerize the oil into a film; they are primarily oxidative. The site of the oxidation is the unsaturation in the molecule so that these behave as olefins rather than esters, and the chemistry of the oxidative degradation is similar in many respects to that of rubber and other unsaturated polymers.

The classic researches of Bolland and Gee (1, 2) and Farmer (3) have demonstrated that the absorption of oxygen by ethyl linoleate leads to the formation of hydroperoxides which decompose to yield various radical products, which may, in turn, induce low molecular weight vinyl polymerization. These steps are represented by the reaction schemes given in Tables I and II. The termination steps are the same in both cases, and whether 2R· radicals or 2ROO·

TABLE I
Mechanism for Hydroperoxide Formation

Initiation				
RH	+ O_2	⟶	R·	+ ·OOH
Propagation				
R·	+ O_2	⟶	ROO·	
ROO·	+ RH	⟶	ROOH	+ R·
Termination				
R·	+ R·	⟶	RR	
ROO·	+ R·	⟶	ROOR	
ROO·	+ ROO·	⟶	ROOR	+ O_2

$R = CH_3(CH_2)_4CH{=}CH{-}\dot{C}H{-}CH{=}CH(CH_2)_7COOEt$

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TABLE II

Mechanism for Hydroperoxide Decomposition in Dilute Solution

$2\ ROOH \longrightarrow \text{Radicals}$

$R\cdot + O_2 \longrightarrow ROO\cdot$

$ROO\cdot + RH \longrightarrow ROOH + R\cdot$

$R\cdot + R\cdot \longrightarrow RR$

$R\cdot + ROO\cdot \longrightarrow ROOR$

$ROO\cdot + ROO\cdot \longrightarrow ROOR + O_2$

radicals combine will depend upon the abundance of oxygen present since R· will not exist in an appreciable concentration in the presence of oxygen. These termination steps are also polymerizing steps, leading to the formation of an unsaturated product. But the decomposition of the hydroperoxide may also activate the double bonds to yield vinyl polymerization with a decrease in unsaturation (Table III).

TABLE III

Polymerization Reactions

$R\cdot + R\cdot \longrightarrow RR$

$ROO\cdot + R\cdot \longrightarrow ROOR$

$ROO\cdot + ROO\cdot \longrightarrow ROOR + O_2$

$R\cdot + C{=}C \longrightarrow RCC\cdot \longrightarrow \longrightarrow$

$ROO\cdot + C{=}C \longrightarrow ROOCC\cdot \longrightarrow \longrightarrow$

In the case of the glyceryl esters they are seen to exhibit a high, if indeterminate, functionality, hence gelation will occur at a very low extent of polymerization, giving very restricted molecular motion and perhaps producing differences in the extent and nature of the film-forming reactions at different depths in the film. As the cross-linking reaction proceeds, the network becomes tighter, and a tough visco-elastic film is produced. If one could stop the reaction at this point, all would be well, but this is impossible since this does not correspond to any sort of equilibrium situation. The process, essentially oxidative, continues, though at a much reduced rate, and loss of weight rather than a gain is observed, also loss of elasticity and embrittlement, among other symptoms of degradation. Loss of elasticity is attributable to a decrease in the segment length between cross-links; the cross-linking reaction has proceeded beyond the optimum. Loss of film strength and loss of weight however are attributable to chain-scission processes. Some of the most typical chain-scission or depolymerization reactions are listed in Table IV. This may seem a formidable series of simultaneous reactions; it is nonetheless a gross oversimplification of the many reactions which can and do occur. Loss of film strength is indicative of internal scission; loss of weight is caused by scission near terminal groups to produce volatile products. Assuming that scission is random, one would expect a constant increase in the fraction of scission that is terminal as the proportion of terminal groups increases. However since each of the reactive species can and does exist in a variety of environments, a fairly continuous spectrum of reactivities is produced, and the film becomes more stable, reacts more slowly, than one would predict from the residual concentration of reactive groups. This is illustrated by some data on the rate of erosion of oil-modified alkyds (4). The rate was independent of the film thickness at any particular time, indicating a bulk reaction, but the rate constant decreases with time, indicating the preferential consumption of the more reactive groups (Figure 1).

TABLE IV

Depolymerization Reactions

$RCH_2OOR \longrightarrow RCH_2O\cdot + \cdot OR$

$RCH(OOH)R \longrightarrow RCHO + \cdot OH + \cdot R$

$RCH_2CH(OOH)R \longrightarrow H_2O + RCH_2COR \longrightarrow RCOCOR \longrightarrow RCO\cdot + \cdot OCR$

$RCH_2COR \xrightarrow{h}{}_2\ CH_3COR + \text{Olefin}$, etc.

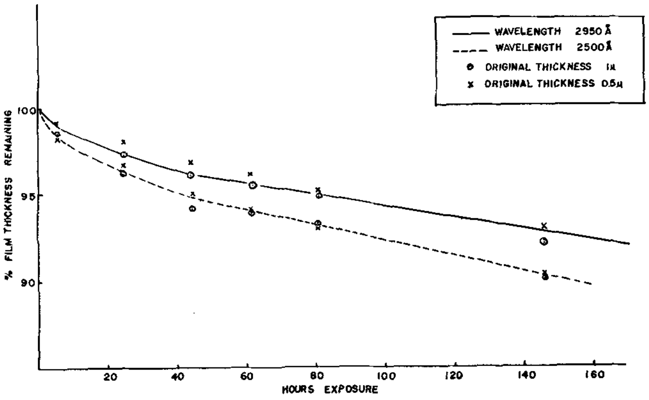

FIG. 1. Rate of film loss at various wavelength distributions.

ANY CONSIDERATION of the oxidative degradation of drying oil films as it is encountered outside the laboratory must include the effect of ultraviolet light. In principle, one may dismiss this added factor as merely a catalyst in the initiation steps. In practice however it is not so simple. Two factors must be considered: the wavelength and the intensity of the irradiation. The wavelength, or more accurately, the wavelength distribution, must approximate the distribution of sunlight, or the results may be altogether different. This is illustrated in Figures 2 and 3, which show the changes in functional group concentrations, as obtained by infrared spectroscopy, when an oil-modified alkyd film is exposed to different wavelengths of ultraviolet light. Short wavelengths, below the atmospheric cut-off, produce different reactions as well as an increase in the rate of decomposition. Having obtained a suitable distribution of

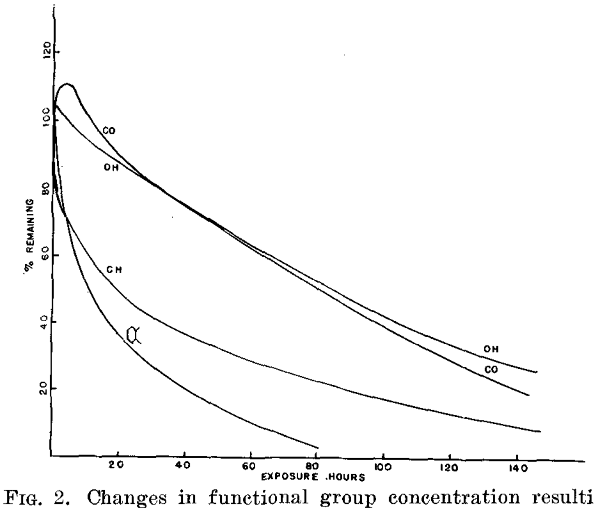

FIG. 2. Changes in functional group concentration resulting from exposure to unfiltered light.

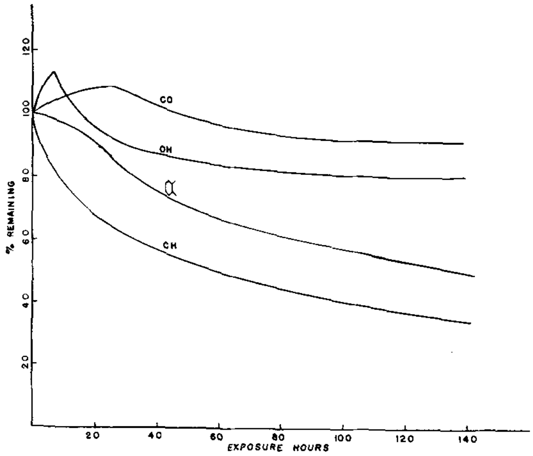

FIG. 3. Changes in functional group concentration resulting from exposure to wavelengths >2500 Å.

wavelengths, the effect of the radiation will be proportional to the amount absorbed, and this, in turn, depends upon the amount of light incident and the absorptivity of the medium (5). So the catalytic effect will be uniform through a film only for a polymer that is completely transparent, in which case the effect will be nil, or for an infinitely thin film. Drying oil films fulfill neither of these requirements, and so a reaction gradient through the film and perhaps a variation in the extent of cross-linking and scission, hence in mechanical properties through the film, is to be expected. Thus any description of the chemical or physical properties at any give time must represent average properties and will depend upon the thickness of the film.

For example, in a study of the gaseous products evolved upon irradiation it was shown that the surface was evolving products having a lower over-all H/C ratio than the interior of the film. A high hydrogen content (as H_2O principally) in the volatile products indicates a predominance of cross-linking reactions. Carbon is present primarily in the backbone of the polymer, so carbon oxides in the volatile products represent successive chain-scission reactions. The effect of this nonuniformity upon the mechanical properties of a film leads to results that sometimes seem impossible. For example, suppose one has a free film which is subject to photo-oxidative drying and degradation, leading finally to loss of elasticity and embrittlement. Since mechanical properties are largely bulk properties, one might attempt to extend the life of the film by adding an ultraviolet screening agent. One can write a mathematical expression predicting the increased time required to absorb the same amount of light and presumably reach the same degree of degradation (6). But consider the effect of the sharply attenuated light intensity; the photocatalyzed cross-linking and degradation will both be attenuated sharply beneath the surface, possibly giving a rigid surface as extensively cross-linked as before and a much less cross-linked interior. Now an applied stress is borne altogether by the surface which, being thin, has a very limited strength. Once it breaks, all of the stress is concentrated at the break and the inner polymer yields. Thus mechanical measurements of percentage elongation at break and tensile strength could be abnormally low, perhaps even lower than the unmodified polymer. This is an extreme, even artificial case, yet it illustrates the sort of results one can obtain when investigating such complex materials.

PERHAPS THE HAZARDS of chemical and mechanical studies of drying oil films have been unduly stressed. Yet the hazards of accelerated weathering tests are no less formidable. The effect of temperature in an oxidation reaction sequence is interesting and serves to illustrate the hazards that must be considered in designing an accelerated weathering cycle. Heat will accelerate a reaction more or less, depending upon the energy of activation of the reaction. Thus the rate of thermal production of radicals from inert molecules is very dependent on temperature, but the subsequent reaction of radicals is not. Whether these radicals combine with oxygen or attack other inert molecules will depend, for example, upon the concentration of oxygen at that site in the film. The passage of oxygen into the film may be an activated process with a low energy of activation (7), or it may be a diffusion process depending on the velocity of the molecules which increases only as the square root of the absolute temperature. In either event the reaction may be oxygen-limited—hence distinctly different at high temperatures than at low temperatures. Photochemical activation presents the same problem. The photochemical steps are temperature-independent; yet if the irradiation produces radicals at a rate such that the film becomes less than saturated in oxygen, one will have introduced a change in kind rather than rate of reaction. Since, for some chain reactions, oxygen acts as an inhibitor and for others as an accelerator, one may expect polymers to accelerate their rate of deterioration more or less than the acceleration predictable from the increase in ultraviolet dosage over natural sunlight. This might suggest that sound accelerated weathering-procedure requires an intensity of ultraviolet radiation not substantially greater than the natural maximum intensity. But since this can be maintained around the clock, day after day, acceleration factors of 10–20 should still be possible.

In addition to the effect upon the chemistry of polymer degradation, unrealistic temperatures may induce mechanical strains which are not encountered in practice; or, for thermoplastic materials, naturally-occurring stress might be relieved by heating above the glass temperature. The whole subject of stresses in films, especially in films deposited on a substrate, has only recently begun to receive the attention that it merits in the total description of film degradation. Inoue (8) has measured the contractive stress caused by heat-curing of resinous coatings by depositing films on flexible metal foil and observing the curvature after permanent set. Linseed oil films may be visualized as a felt-like material, on a molecular scale, with its highly cross-linked triglyceride polymers intertwined. At the gel point, even at the tack-free point, there exists a significant amount of uncombined material. As this polymerizes, there will be some shrinkage, and the polymer, as it becomes more firmly cross-linked, will be unable to shrink so that voids, and stresses, will develop even without a change in temperature. The development of strain in a film, particularly when accompanied by surface embrittlement, leads to mechanical failure in the form of cracking or perhaps loss of adhesion.

Degradation of linseed oil films, being essentially oxidative, changes the response of the film to moisture and other solvents. As the films oxidize, they develop a larger fraction of water-sensitive functional groups, but, acting in opposition to this, is the over-all increase in the extent of cross-linking, which limits the ability of the film to absorb water or even organic solvents. When weathered and unweathered films are swelled in water, Browne (9) observed that unweathered films swell by the volume of water absorbed, but weathered films swell less than the volume absorbed, indicating that there was a substantial void content in the weathered film. Browne also found that films supported on a nonpermeable substrate swell less than free films, indicating the importance of compressive stress in altering the equilibrium. Swelling of films in water and its relation to loss of adhesion has been studied by d'Ans (10), who has measured the equilibrium concentration of water, the time required to reach equilibrium, and the time until detachment of the films from the substrate as functions of drying time, relative humidity, use of driers, and exposure to ultraviolet light.

While there is the compressive strain when the film swells more than the substrate, there may also be a contractive strain when the substrate is wood or some other water-sensitive material. This becomes increasingly more important as the film ages and becomes less subject to swelling. This film may also become less permeable as it degrades, assuming no mechanical failure in the film. If there is a large difference in the rate of diffusion of water between a water-sensitive substrate and a film, there can result an accumulation of water in the interface with the subsequent loss of adhesion between the substrate and the film.

The increase of oxygenated groups, particularly at the surface of the weathered film, has an obvious effect on the wettability of the surface. The contact angle of water on a freshly prepared linseed oil film is often greater than 90 degrees; after periods of exposure to ultraviolet light the contact angle decreases until finally water spreads freely on the surface, making all the microscopic fissures accessible to the liquid water and accelerating the erosive action of the water. When weathered films are immersed in water, then dried and weighed, it is found that there is a much greater loss of weight than when unweathered films are similarly treated. It seems to make little difference whether the films are irradiated and immersed simultaneously or sequentially. From these facts and from a study of the chemical composition of the aqueous extract, it seems quite certain that water does not enter chemically into the degradation reactions but leaches out soluble, highly oxygenated, degradation products and contributes to mechanical stresses in the film or at the film substrate interface.

There are other factors in degradation, but generally they are important only in special situations. Almost all linseed oil films will be subject to the action of heat, light, oxygen, and water; chemical reactions will occur and these will manifest themselves in physical changes. Much of our knowledge is inexact, perhaps based upon grossly simplified chemical or mechanical models. While the work upon linoleate esters in dilute solution is valid and pertinent to the oxidation of linseed oil, this is not sufficient to describe the process in the film quantitatively. Fortunately there exists an increasingly large number of experimental approaches which will ultimately yield the necessary information. Chemical studies have come to rely more and more upon instrumental, particularly spectroscopic, techniques, for obvious reasons. They are nondestructive procedures, require only minute quantities of material, and frequently are not handicapped by the insolubilization of the polymer. Ultraviolet spectroscopy has been invaluable in studies of the isomerization of double bonds, and infrared spectroscopy has become the standard procedure for identifying functional groups consumed and formed in the oxidative process. These have undergone numerous refinements in the hands of successive workers. Differential spectroscopy has been used to make small changes in composition more evident. Related functional groups, such as alcoholic and hydroperoxide OH groups which could not be separated unambiguously in the conventional 2–15 micron region of the spectrum, have been resolved in the near infrared. Loss of weight measurements may be made more accurately with new recording balances. Changes in film thickness for films of any thickness may be made with a Tolansky interferometer or upon clear thin (less than 10,000 Ångstroms) films from their specular reflectance spectra. In particular, the combination of transmission and reflectance, as shown in Figure 4, gives an excellent quantitative measure of the changes in thickness and absorption before and after irradiation (11).

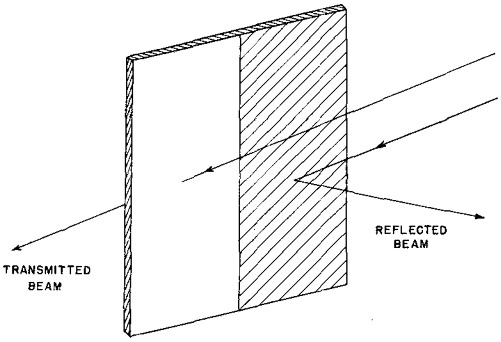

Fig. 4. Half-chromium-plated silica slides.

Gas chromatography should be useful in analyzing the volatile decomposition products more accurately than has been previously possible, perhaps to permit a description of the ratio of scission to cross-linking reactions as a function of film thickness. Such data should eventually yield a reaction profile across the film as a chemical counterpart of the mechanical properties gradient which will be obtained from mechanical measurements at low stress. This does not argue against the obvious utility of the conventional tensile strength and elongation at break measurements, but catastrophic failure is not the point at which one studies most directly the mechanical properties of any simple substance, much less such a grossly inhomogeneous one like a linseed oil film. Studies of permanent set, damping, relaxation under constant extension, extension under constant load, as functions of film thickness and previous history, and interpreted in the light of the constantly developing mathematical theory of visco-elastic materials will eventually give us an exact description of mechanical failure in films and perhaps suggest the most fruitful experimental approaches toward solving this.

Swelling measurements are a likely approach to a study of the change in the extent of cross-linking in a film. Permeability studies also reflect the degree of cross-linking and the chemical composition of the film. In this particular field much of the work in the literature does not distinguish between true molecular transport through the film and gross diffusion of liquids or gases through mechanical defects in the film. Admittedly the probability of obtaining and maintaining a perfectly continuous film does depend on the polymer itself, the method of film preparation, the film thickness, the extent of degradation; and this is a problem worthy of study, but no useful purpose is served in confusing this with permeability. In the case of many polymers the hazards of film defects are such that a valid permeability experiment must demonstrate the absence of gross transfer.

Another whole area of properties which are affected by degradation are the electrical properties of a film. These have been studied most frequently by workers concerned with corrosion protection. Electrical measurements provide an excellent check on film continuity, and this is frequently valuable information. It is certainly true that the degradation of a film affects its electrical impedance, particularly in the presence of absorbed water, but the relation of these quantities to other chemical or physical data is beyond our present limitations of theory so that electrical measurements must remain an empirical though convenient method for following degradation.

In summary, the basic chemistry of linseed oil oxidation is well known, but the detailed quantitative description of the process in the film is uncertain. That this process leads to a film of complex chemical and mechanical properties has been demonstrated in theory and practice. Further progress in this field may suggest routes to more desirable films.

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Chemical Intermediates and Derivatives from Unsaturated Oils and Acids

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THE SUBJECT for discussion is essentially that of the reactions of unsaturated fatty acids. Such fatty acids have two main points of reaction or reactive centers which are, of course, the carboxyl group and the unsaturated hydrocarbon chain having one or more carbon-to-carbon double bonds. Linoleic acid provides a good example of these reactive points.

Reactions involving the carboxyl group are many and varied and are used to provide a large group of commercially important products. These reactions include those of salt or soap formation, esterification, amidation, nitrile formation, amination, acid chloride formation, and many others. Even though this group of reactions would fall under the scope of this paper and numerous industrial organizations or enterprises are based on them, the only concern will be with the reactions of unsaturated fatty acids or their derivatives that occur at or are induced by the carbon-to-carbon double bonds present in the relatively long hydrocarbon chains. The reactions are, in general, fairly typical of those entered into by other non-terminal olefinic materials.

For the sake of simplicity, reactions of the double bonds or those induced by double bonds will be classified in the following four main categories:

a) the addition of chemical reagents across the double bond;
b) the reactions in which cleavage of the hydrocarbon chain at the double bond occurs to give lower molecular weight products;
c) the reactions in which isomerization of the double bond occurs; this may be geometric (oleic acid, which is the *cis* isomer, and elaidic acid, the *trans* isomer) or positional (oleic acid, which is Δ-9, and petroselenic acid, which is Δ-6) isomerization, or skeletal (oleic acid and 11-methyl-7-heptadecenoic acid) rearrangement, or a combination of these.
d) the reactions that do not take place at the double bond but do occur because they are induced by its proximity, such as reactions at carbons 8 and 11 in oleic acid and at carbons 8, 11, and 14 in linoleic acid.

In the case of linoleic acid carbon atom number 11 has the larger reaction potential because both double bonds have an influence on the reaction point.

An attempt will now be made to examine a number of processes, many of them practiced commercially today, and to show that they usually can be interpreted in the light of one or more of the above-mentioned type of reactions. Where possible, commercial utilization of the end products from such reactions or processes will be mentioned or described. It is believed that of special interest will be those processes and products which compete more or less directly with the corresponding ones in and of the conventional drying-oil industry.

Chemical Reactions of Unsaturated Oils and Their Fatty Acid Components

Addition Reactions. Chemical reactions in which two fragments add across a carbon-to-carbon double bond are quite common and numerous. Some of them are used for analytical purposes only, whereas others are used to prepare materials which are of considerable commercial significance. A partial list of such reactions would include the following where, for illus-